

Some Rigorous Results Relating Nonequilibrium, Equilibrium, Calorimetrically Measured and Residual Entropies during Cooling

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Abstract

We use rigorous nonequilibrium thermodynamic arguments to establish that (i) the nonequilibrium entropy $S(T_0)$ of any system is bounded below by the experimentally (calorimetrically) determined entropy $S_{\text{expt}}(T_0)$, (ii) $S_{\text{expt}}(T_0)$ is bounded below by the equilibrium or stationary state (such as the supercooled liquid) entropy $S_{\text{SCL}}(T_0)$ and consequently (iii) $S(T_0)$ cannot drop below $S_{\text{SCL}}(T_0)$. It then follows that the residual entropy S_R is bounded below by the extrapolated $S_{\text{expt}}(0) > S_{\text{SCL}}(0)$ at absolute zero. These results are very general and applicable to all nonequilibrium systems regardless of how far they are from their stationary states.

I. INTRODUCTION

Nonequilibrium states like glasses from supercooled liquids (SCLs) are abundant in Nature, whose entropy S can only be estimated by calorimetrically measured entropy S_{expt} , which can then be extrapolated to absolute zero. The extrapolated value S_R at absolute zero is commonly known as the *residual entropy* and is normally found to satisfy $S_R > 0$. In practice, one considers the isobaric entropy $S(T_0)$ of the system as a function of the temperature T_0 of the surrounding medium; see Fig. 1. The existence of S_R was first theoretically demonstrated by Pauling and Tolman [1]; see also Tolman [2]. In addition, the existence of the residual entropy has been demonstrated rigorously for a very general spin model by Chow and Wu [3]. The residual entropy for glycerol was observed by Gibson and Giauque [4] and for ice by Giauque and Ashley [5]. Pauling [6] provided the first numerical estimate for the residual entropy for ice, which was later improved by Nagle [7]. Nagle's numerical estimate has been recently verified by simulation [8, 9]. The numerical simulation carried out by Bowles and Speedy [10] for glassy dimers also supports the existence of a residual entropy. For a brief review of the history of the residual entropy, see [11–18]. Thus, it appears that the support in favor of the residual entropy, see the curve Glass1 in see Fig. 2, is quite strong. Its existence also does not violate Nernst's postulate, as the latter is applicable only to true equilibrium states with a *non-degenerate* ground state [19–21]. Indeed, many exactly solved statistical mechanical models show a non-zero entropy at absolute zero. However, as of yet, no experiment can be performed at absolute zero to experimentally determine the residual entropy; in all cases, some sort of *extrapolation* is required. This point should not be forgotten in the following whenever we speak of the residual entropy. Despite the above mentioned support for the reality of the residual entropy, it has become a highly debated issue in the literature [22–28] as discussed by these authors. The reason for the

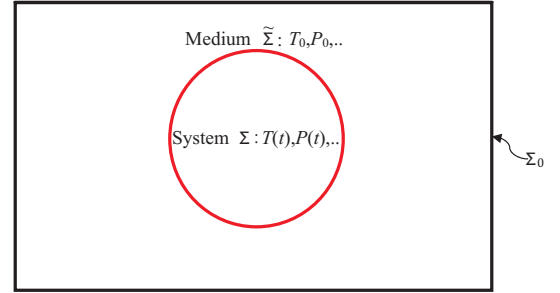


FIG. 1: An isolated system Σ_0 consisting of the system Σ in a surrounding medium $\tilde{\Sigma}$. The medium and the system are characterized by their fields T_0, P_0, \dots and $T(t), P(t), \dots$, respectively, which are different when the two are out of equilibrium.

debate is that the relationship among $S(T_0)$, $S_{\text{expt}}(T_0)$ and the entropy $S_{\text{SCL}}(T_0)$ of the corresponding stationary state is not well understood, and understanding this relationship is the main theme of this work.

In the following, we will speak of "the equilibrium" state associated with a nonequilibrium state as the stationary (time-independent) state. Depending on the context, the equilibrium state may represent a true equilibrium state such as a crystal or a stationary metastable state such as the supercooled liquid. A nonequilibrium state in this work will always be taken as time-dependent. Accordingly, $S(T_0)$ above should be correctly expressed as $S(T_0, t)$, and in some cases can be expressed as a function $S(T(t))$ of the instantaneous temperature $T(t)$ [29–31] of the system; see Fig. 1. In this work, we will not be concerned with $T(t)$. Thus, we will simply use $S(T_0)$ for the nonequilibrium state, knowing well that the state continues to change with time.

For the purpose of clarity, we will consider supercooled liquids and associated nonequilibrium states (glasses) in the following, but the arguments are applicable to all nonequilibrium states. The supercooled liquid undergoes a glass transition over a transition range, see Fig. 2, over which the entropy falls rapidly with lowering temperature T_0 . The transition region is controlled by the

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rate of cooling so that the glass is a nonequilibrium state [31, 32]. As the irreversibility due to the glass transition does not allow for an exact evaluation of the entropy, it has been suggested [27, 28] that the entropy decreases by an amount almost equal to S_R within the glass transition region so that the glass (see Glass2 in Fig. 2, whose entropy lies below the supercooled liquid) would have a vanishing entropy at absolute zero. It has been shown by Goldstein [11] that Glass2 results in a violation of the second law. It should be stressed that if there is ever any *conflict* between the second law [33] and any other law in physics such as the zeroth or the third law, it is the second law that is believed to hold in *all* cases. One can also argue that to confine the glass into a *unique* basin in the energy landscape requires *microscopic* information [15, 32, 34]; hence, the particular glass *cannot* be considered in a macrostate. Oppenheim [35] has also raised somewhat of a similar objection.

We have drawn the two entropy curves (Glass1 or Glass2) in Fig. 2 that emerge out of the entropy curve for the equilibrated supercooled liquid for a given τ_{obs} in such a way that Glass1 has its entropy above (so that $S_R \geq 0$) and Glass2 below (so that $S_R \equiv 0$) that of the supercooled liquid. The entropy of Glass1 (Glass2) approaches that of the equilibrated supercooled liquid entropy from above (below) during isothermal relaxation (fixed temperature of the medium) relaxation; see the two downward vertical arrows for Glass1. It is the approach to equilibrium that distinguishes the two glasses, Glass1 and Glass2. Almost all experimental investigations leave open the possibility that Glass2 may materialize if the irreversibility is too large. Our work clarifies the situation.

It is abundantly clear from the above discussion that there is a need to look at the relationship between various entropies in Fig. 2. As is customary, we treat the supercooled liquid as an equilibrium state, even though it not a true equilibrium state; see above. We proceed by following the strict second law inequality $d_i S > 0$ [29, 30, 36, 37], see Eq. (4), and use it to prove the following results applicable to *all* nonequilibrium systems, regardless of how close or far they are from their equilibrium state:

1. Various entropies obey the following strict inequalities

$$S(T_0) > S_{\text{expt}}(T_0) > S_{\text{SCL}}(T_0) \quad \text{for } T_0 < T_{0g}, \quad (1)$$

so that the entropy variation in time has a unique direction as shown by the *downward arrows* in Fig. 2. Thus, $S(T_0)$ cannot drop below $S_{\text{SCL}}(T_0)$ (such as Glass2 in Fig. 2) without violating of the second law [33].

2. The experimentally observed non-zero entropy at absolute zero in a vitrification process is a *strict lower bound of the residual entropy* of any system:

$$S_R \equiv S(0) > S_{\text{expt}}(0) > S_{\text{SCL}}(0). \quad (2)$$

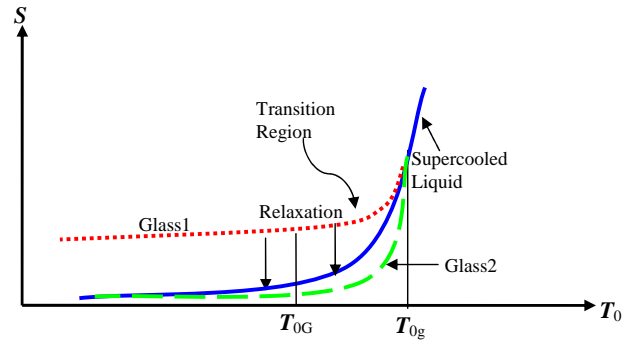


FIG. 2: Schematic behavior of the entropy of the equilibrated, i.e. stationary supercooled liquid (solid curve) and two possible glasses (Glass1-dotted curve, Glass2-dashed curve) during vitrification. The transition region between T_{0g} and T_{0G} has been exaggerated to highlight the point that the glass transition is not a sharp point. For all temperatures $T_0 < T_{0g}$, any nonequilibrium state undergoes isothermal structural relaxation in time towards the supercooled liquid. The entropy of the supercooled liquid is shown to extrapolate to zero per our assumption, but that of Glass1 to a non-zero value and of Glass2 to zero at absolute zero.

The Eq. (1) is consistent with Glass1 but not with Glass2. All experiments on or exact/approximate computations for nonequilibrium systems *must* obey the strict inequalities in Eqs. (2-1) without exception. This is the meaning behind the usage of "... rigorous ..." in the title. The actual values of the entropy are not relevant for the aim of this work, which is to find the relationship among different entropies under vitrification. Because of the possibility that the systems may be far away from equilibrium such as in a fast quench, where the irreversible contributions may not be neglected, our results go beyond the previous calorimetric evidence [12, 13, 18, 23]. The systems we are interested in include glasses and imperfect crystals as special cases. However, to be specific, we will only consider glasses below.

II. ENTROPY BOUNDS DURING VITRIFICATION

The vitrification process we consider is carried out at some cooling rate as follows. The temperature of the medium is isobarically changed by some small but fixed $\Delta T_0 < 0$ from the current value to the new value, and we wait for (not necessarily fixed) time τ_{obs} at the new temperature to make an instantaneous measurement on the system before changing the temperature again. At some temperature T_{0g} , see Fig. 2, the relaxation time τ_{relax} , which continuously increases as the temperature is lowered, becomes equal to τ_{obs} . Just below T_{0g} , the structures are not yet frozen; they "freeze" at a lower

temperature T_{0G} (not too far from T_{0g}) to form an amorphous solid with a viscosity close to 10^{13} poise. This solid is identified as a *glass*. The location of both temperatures depends on the rate of cooling, i.e. on τ_{obs} . Over the glass transition region between T_{0G} and T_{0g} in Fig. 2, the system gradually turns from an equilibrium supercooled liquid at or above T_{0g} into a glass at or below T_{0G} [31, 32, 38]. We overlook the possibility of the supercooled liquid ending in a spinodal [39]. It is commonly believed that $S_{\text{SCL}}(0)$ will vanish at absolute zero ($S_{\text{SCL}}(0) \equiv 0$), as shown in the figure. However, it should be emphasized that the actual value of $S_{\text{SCL}}(0)$ has no relevance for the theorems below.

We will only consider isobaric cooling (we will not explicitly exhibit the pressure in this section), which is the most important situation for glasses. The process is carried out along some path from an initial state A at temperature T_0 in the supercooled liquid state which is still higher than T_{0g} to the state A_0 at absolute zero. The state A_0 depends on the path $A \rightarrow A_0$, which is implicit in the following. The change dS between two neighboring points along such a path is $dS = d_e S + d_i S$ in modern notation [29, 30, 36, 37, 40, 41]. The component

$$d_e S(t) = d_e Q(t)/T_0 \equiv C_P dT_0/T_0 \quad (3)$$

represents the reversible entropy exchange with the medium in terms of the exchange heat $d_e Q(t)$ (in keeping with the modern notation) added to the glass by the medium at time t to the medium at T_0 and the heat capacity C_P . It also represents the *calorimetrically* determined change in the entropy in any process. The component

$$d_i S > 0 \quad (4)$$

represents the irreversible entropy generation within the system in the irreversible process, and contains, in addition to the contribution from the irreversible heat transfer with the medium, contributions from all sorts of viscous dissipation going on *within* the system and normally require the use of internal variables [29, 30, 36, 40, 41]. The equality in Eq. (4) holds for a reversible process, which we will no longer consider unless stated otherwise. A discontinuous change in the entropy is ruled out from the continuity of the Gibbs free energy G and the enthalpy H in vitrification proved elsewhere [29]. Thus, we only consider a continuous change in the entropy as shown by the two glass curves in Fig. 2.

Theorem 1 *The experimentally observed (extrapolated) non-zero entropy at absolute zero in a vitrification process is a strict lower bound of the residual entropy of any system:*

$$S_R \equiv S(0) > S_{\text{expt}}(0).$$

Proof. We have along $A \rightarrow A_0$

$$S(0) = S(T_0) + \int_A^{A_0} d_e S + \int_A^{A_0} d_i S, \quad (5)$$

where we have assumed that there is no latent heat in the vitrification process. Since the second integral is always *positive*, and since the residual entropy S_R is, by definition, the entropy $S(0)$ at absolute zero, we obtain the important result

$$S_R \equiv S(0) > S_{\text{expt}}(0) \equiv S(T_0) + \int_{T_0}^0 C_P dT_0/T_0. \quad (6)$$

This proves Theorem 1. The integral represents the calorimetric contribution. ■

The strict forward inequality above clearly establishes that the residual entropy at absolute zero must be strictly larger than $S_{\text{expt}}(0)$ in any nonequilibrium process.

Theorem 2 *The calorimetrically measured (extrapolated) entropy during processes that occur when $\tau_{\text{obs}} < \tau_{\text{relax}}(T_0)$ for any $T_0 < T_{0g}$ is larger than the supercooled liquid entropy at absolutely zero*

$$S_{\text{expt}}(0) > S_{\text{SCL}}(0).$$

Proof. Let $\dot{Q}_e(t) \equiv d_e Q(t)/dt$ be the rate of net heat loss by the system. For each temperature interval $dT_0 < 0$ below T_{0g} , we have

$$\begin{aligned} |d_e Q| &\equiv C_P |dT_0| = \int_0^{\tau_{\text{obs}}} \left| \dot{Q}_e \right| dt < |dQ|_{\text{eq}}(T_0) \\ &\equiv \int_0^{\tau_{\text{relax}}(T_0)} \left| \dot{Q} \right| dt, \quad T_0 < T_{0g} \end{aligned}$$

where $|dQ|_{\text{eq}}(T_0) > 0$ denotes the net heat loss by the system to come to equilibrium, i.e. become supercooled liquid during cooling at T_0 . For $T_0 \geq T_{0g}$, $d_e Q \equiv d_e Q_{\text{eq}}(T_0) \equiv C_{P,\text{eq}} dT_0$. Thus,

$$\int_{T_0}^0 C_P dT_0/T_0 > \int_{T_0}^0 C_{P,\text{eq}} dT_0/T_0.$$

We thus conclude that

$$S_{\text{expt}}(0) > S_{\text{SCL}}(0). \quad (7)$$

This proves Theorem 2. ■

The strict inequalities above are the result of glass being a nonequilibrium state. We have now verified the second statement in the Introduction.

The difference $S_R - S_{\text{expt}}(0)$ would be larger, more irreversible the process is. The quantity $S_{\text{expt}}(0)$ can be determined calorimetrically by performing a cooling experiment. We take T_0 to be the melting temperature T_{0M} , and uniquely determine the entropy of the supercooled liquid at T_{0M} by adding the entropy of melting to the crystal entropy $S_{\text{CR}}(T_{0M})$ at T_{0M} . The latter is obtained in a unique manner by integration along a reversible path from $T_0 = 0$ to $T_0 = T_{0M}$:

$$S_{\text{CR}}(T_{0M}) = S_{\text{CR}}(0) + \int_0^{T_{0M}} C_{P,\text{CR}} dT_0/T_0,$$

here, $S_{\text{CR}}(0)$ is the entropy of the crystal at absolute zero, which is traditionally taken to be zero in accordance with the third law, and $C_{P,\text{CR}}(T_0)$ is the isobaric heat capacity of the crystal. This then uniquely determines the entropy of the liquid to be used in the right hand side in Eq. (6). We will assume that $S_{\text{CR}}(0) = 0$. Thus, the experimental determination of $S_{\text{expt}}(0)$ is required to give the *lower bound* to the residual entropy in Eq. (2). Experiment evidence for a non-zero value of $S_{\text{expt}}(0)$ is abundant as discussed by several authors [4, 5, 11–13, 23]; a textbook [38] also discusses this issue. Goldstein [11] gives a value of $S_{\text{R}} \simeq 15.1$ J/K mol for *o*-terphenyl from the value of its entropy at $T_0 = 2$ K. We have given above a mathematical justification of $S_{\text{expt}}(0) > 0$ in Eq. (7). The strict inequality proves immediately that the residual entropy *cannot* vanish for glasses, which justifies the curve Glass1 in Fig. 2.

The inequality in Eq. (6) takes into account any amount of irreversibility during vitrification; it is no longer limited to only small contributions of the order of 2% considered by several others [11, 14, 18, 38, 42], which makes our derivation very general.

By considering the state A_0 above to be a state A_0 of the glass in a medium at some arbitrary temperature T'_0 below $T_{0\text{g}}$, we can get a generalization of Eq. (6):

$$S(T'_0) > S_{\text{expt}}(T'_0) \equiv S(T_0) + \int_{T_0}^{T'_0} C_P dT_0/T_0. \quad (8)$$

We again wish to remind the reader that all quantities depend on the path $A \rightarrow A_0$, which we have not exhibited. By replacing T_0 by the melting temperature $T_{0\text{M}}$ and T'_0 by T_0 , and adding the entropy $\tilde{S}(T_{0\text{M}})$ of the medium on both sides in the above inequality, and rearranging terms, we obtain (with $S_{\text{L}}(T_{0\text{M}}) = S_{\text{SCL}}(T_{0\text{M}})$ for the liquid)

$$S_{\text{L}}(T_{0\text{M}}) + \tilde{S}(T_{0\text{M}}) < S(T_0) + \tilde{S}(T_{0\text{M}}) - \int_{T_{0\text{M}}}^{T_0} C_P dT_0/T_0, \quad (9)$$

where we have also included the equality for a reversible process. This provides us with an independent derivation of the inequality given by Sethna and coworker [17].

It is also clear from the derivation of Eq. (7) that the inequality can be generalized to any temperature $T_0 < T_{0\text{g}}$ with the result

$$S_{\text{expt}}(T_0) > S_{\text{SCL}}(T_0), \quad (10)$$

with $S_{\text{expt}}(T_0) \rightarrow S_{\text{SCL}}(T_0)$ as $T_0 \rightarrow T_{0\text{g}}$ from below. Thus, $S_{\text{expt}}(T_0)$ appears to have a form similar to that of Glass1 in Fig. 2 but strictly lying below it. We have now verified the first statement in the Introduction.

While we have only demonstrated the forward inequalities, the excess $S_{\text{R}} - S_{\text{expt}}(0)$ can be computed in nonequilibrium thermodynamics [29, 30, 36, 40, 41], which provides a clear prescription for calculating the irreversible entropy generation. We do not do this here as we are only interested in general results, while the calculation of irreversible entropy generation will, of course, be system-dependent and will require detailed information. Gutzow and Schmelzer[12] provide such a procedure with a single internal variable but under the assumption of equal temperature and pressure for the glass and the medium. However, while they comment that $d_i S \geq 0$ whose evaluation requires system-dependent properties, their main interest is to only show that it is negligible compared to $d_e S$.

We have proved Theorems 1 and 2 by considering only the system without paying any attention to the medium. For Theorem 1, we require the second law, i.e. Eq. (4). This is also true of Eq. (8). The proof of Theorem 2 requires the constraint $\tau_{\text{obs}} < \tau_{\text{relax}}(T_0)$ for any $T_0 < T_{0\text{g}}$, which leads to a nonequilibrium state. The same is also true of Eq. (10).

III. CONCLUSIONS

We have considered the role of irreversible entropy generation during isobaric vitrification to rigorously justify the two statements in the Introduction. They are valid regardless of how far the system is out of equilibrium. Thus, our results are very general and are not restricted by the small amount of irreversibility that is normally considered in the literature. The first statement shows that the instantaneous entropy $S(T_0, t)$ must always be higher than $S_{\text{expt}}(T_0)$, which in turn must always be higher than $S_{\text{SCL}}(T_0)$ of the equilibrated supercooled entropy. The second statement shows that the extrapolation of the calorimetrically measured entropy to absolute zero forms a strict lower bound to the residual entropy S_{R} . As the former is usually positive, this proves that the residual entropy has to be at least as large as this value. From the first statement, it also follows that Glass2 is not realistic.

The statements follow from considering the thermodynamic entropy that appears in the second law, and their validity is not affected by which equivalent statistical definition of entropy one may wish to use for the thermodynamic entropy, an issue that has been investigated by us recently [37].

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- [33] By the second law we mean the law of increase of the entropy according to which the (thermodynamic) entropy of an isolated system can never decrease. Any statistical interpretation of this law must ensure this law.
- [34] The preparation to get the system in a unique microstate requires knowing precisely the cell C_i a particular particle i belongs to. This should be contrasted with the situation such as in a crystal or a glass, in which, although each particle is confined within a cell, we have no knowledge which particle belongs to this cell. This ambiguity in the microstates is a characteristic of a statistical system [14, 15] that results in a macrostate. The preparation of a unique microstate results in a unique specification and is not physically feasible to accomplish in reality.
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